

Studies on Syntheses and Properties of Episulfide-Type Optical Resins with High Refractive Index

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ABSTRACT: A series of novel high refractive index episulfide-type optical resins were prepared by ring-opening copolymerization of bis(β -epithiopropylthioethyl) sulfide (BEP TES) with episulfide derivative of diglycidyl ether of bisphenol A (ESDG EBA) and 2,4-tolylene diisocyanate (TDI), respectively, in the presence of triethylamine as a curing catalyst. The episulfide monomers, BEP TES and ESGD EBA, were synthesized from their corresponding epoxy compounds, respectively. The cured transparent resins exhibit high refractive index ($n_d > 1.63$) and relatively low dispersion. The refractive index (n_d) and Abbe's number (ν_d) of the BEP TES/ESDG EBA curing system increased linearly with the weight content of BEP TES monomer in the range from 1.633 and 34.0 for the copolymer with 10 wt % of

BEP TES to 1.697 and 38.1 for the homopolymer of pure BEP TES. For the BEP TES/TDI curing system, the refractive index and Abbe's number varied linearly with the molar ratio of BEP TES to TDI from 1.652 and 28.7 to 1.669 and 34.6. High glass-transition temperatures ($T_g > 130^\circ\text{C}$) of the cured BEP TES/TDI resins were observed, which indicate that the cured BEP TES/TDI resins possess a good heat resistance. The optical, physical, and thermal properties of the episulfide-type cured optical resins were also discussed in this study. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 89: 2426–2430, 2003

Key words: episulfide monomer; diisocyanate; copolymerization; refractive index; optical resins

INTRODUCTION

Polymer optical materials have been developed rapidly in recent years and have been used as lenses, optical waveguides, prisms, disk materials, and as substitutes for inorganic glasses.^{1,2} Although the optical resins have the advantages of light weight, excellent impact resistance, good processability, and dyeability compared with glasses, the refractive index of the normally used resins is lower than 1.60. Thus it is desired to develop new types of optical resins with high refractive index, low dispersion, and well-balanced physical properties. Various studies were conducted to develop high refractive index optical materials, including additional polymerization resins,^{3–8} polyethersulfone resins,^{9,10} polythiourethane resins,^{4,11–14} and epoxy-type resins.^{15–19}

Similar to epoxy resins, episulfide-type resins also possess the advantages of chemical resistance, small shrinkage, good heat resistance, and excellent mechanical properties.^{19,20} In addition, episulfide-type

resins contain more sulfur elements, which can increase the refractive index of polymers. Thus episulfide-type optical resins were recently developed as lens materials.^{19,21–26} However, the episulfide-type optical resins obtained by copolymerization of episulfide monomers have not previously been the subject of detailed investigation. In this work a series of novel episulfide-type optical resins were prepared by ring-opening copolymerization of bis(β -epithiopropylthioethyl) sulfide (BEP TES) with episulfide derivative of diglycidyl ether of bisphenol A (ESDG EBA) and 2,4-tolylene diisocyanate (TDI), respectively. The optical, physical, and thermal properties of the prepared optical resins constitute the focus of the present study. The relationships between properties and composition of the copolymerization resins are also discussed.

EXPERIMENTAL

Materials

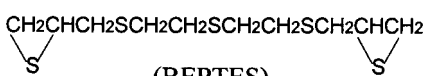
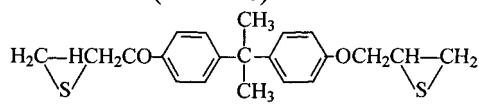
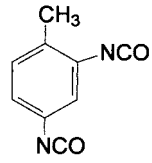
Bis(β -epoxypropylthioethyl) sulfide (DGEMES) was synthesized according to the literature¹⁷ (refractive index, $n_d^{20} = 1.569$). The episulfide derivative of diglycidyl ether of bisphenol A (ESDG EBA) was prepared from diglycidyl ether of bisphenol A (DGEBA) as previously reported²⁷; mp: 89–90°C, $n_d^{20} = 1.61$. Thiourea, 2,4-tolylene diisocyanate (TDI), triethylamine, and other reagents were of analytical grade and were used without further purification.

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TABLE I
Structure and Refractive Index of Episulfide Monomer and Diisocyanate

Structure of episulfide monomer and diisocyanate	Refractive index (n_d^{20})
 <p>(BEPTES)</p>	1.635
 <p>(ESDGEBAs)</p>	1.61
 <p>(TDI)</p>	1.567

Synthesis of BEPTES

BEPTES was synthesized by the method referenced to patent literature.²² DGEMES (100 g), thiourea (118.7 g), acetic anhydride (4 g), toluene (313 mL), and methanol (313 mL) were placed into a 1000-mL four-neck round-bottom flask. The reaction solution was maintained under nitrogen flow on a water bath of 30°C for 10 h. After the reaction was completed, the reaction solution was extracted with toluene. The organic phase was washed with a 1% aqueous sulfuric acid solution and then distilled water until neutral. Finally, the solvents were distilled out under reduced pressure to obtain 80 g of BEPTES as a white solid, yield 71.2%, mp: 56–57°C, $n_d^{20} = 1.635$.

IR (neat), ν (cm^{-1}) 2960, 2923, 2816, 1425, 1244, 1194, 1142, 1088, 1047, 995, 841, 727, 681, 659, 611 (stretching vibration of episulfide three-member ring). ¹H-NMR (CDCl_3): (ppm) 2.2 (d, 2H), 2.6 (d, 2H), 2.65 (dd, 2H), 2.77–2.9 (m, 8H), 3.0 (dd, 2H), 3.1 (m, 2H). ANAL. calcd for $\text{C}_{18}\text{H}_{18}\text{S}_3\text{O}_4$: 298.0. Found: 298.0.

Preparation of transparent optical resins

The episulfide monomer BEPTES was mixed with monomer ESDGEBAs and TDI in the desired ratio at 60°C. Triethylamine (1 wt %) was blended with the above mixtures, respectively. Then, the mixtures were poured into a preheated glass mold with rubber gasket (the glass mold was treated with release agent). The glass mold and the mixture sealed inside were heated at 65°C for 4 h, at 80°C for 2 h, at 100°C for 2 h, at 120°C for 0.5 h, after which the oven was turned off. After the temperature of the oven decreased to room temperature, the mold was removed from the cured resin and a transparent resin plate was obtained.

Characterization and measurement

Structure characterization of episulfide monomers

FTIR spectra were recorded on a Nicolet AVATAR360 FTIR spectrometer (Nicolet Instruments, Madison, WI). ¹H-NMR spectra were obtained from a unity-400NMR in CDCl_3 solution using tetramethylsilane as an internal reference. Elemental analysis (EA) was performed by a Perkin–Elmer 2400 series II analyzer Perkin Elmer Cetus Instruments, Norwalk, CT). The molecular weight was measured on a 4150 mass spectrometer (Finniganmat Corp., New York).

Property measurement of transparent cured resins

Refractive index and Abbe's number. The refractive indices (n_d) of the cured resins were measured by a WZS-1 refractometer (Shanghai Optical Instrument Factory, Shanghai, China) at 20°C. The Abbe's numbers (ν_d) of the cured resins were calculated from a dispersion table.

Entire light transmittance. The entire light transmittance of cured resins was measured by use of a hazemeter in accordance with ASTM D1003-59.

Surface hardness. Surface hardness was evaluated by pencil hardness. The cured resin sheets were scratched by a pencil at an angle of 45° using 1 kg of weight. The hardest pencil that did not scratch the test piece was assigned as its hardness.

Thermal properties. Glass-transition temperatures of the cured resins were obtained from a Perkin–Elmer DSC7 in nitrogen atmosphere at a heating rate of 10°C/min.

TABLE II
Properties of Cured BEPTES/ESDGEBA Resins

BEPTES (wt %)	n_d^{20}	ν_d	ρ (g/cm ³)	Rwa^a (wt %)	Hard ^b	T_g^c (°C)	$T\%^d$	US ^e (nm)	YI ^f
10	1.633	34.0	1.241	0.108	4H-5H	150	84	358	2.0
25	1.642	34.6	1.247	0.210	4H	136	85	344	2.2
50	1.657	35.5	1.290	0.236	3H	—	82	347	3.7
75	1.668	36.6	1.301	0.272	2H	126	86	350	1.9
90	1.681	37.4	1.336	0.301	2H	—	82	343	2.9
100	1.697	38.1	1.354	0.325	H-2H	65	80	325	2.0

^a Rwa , water absorption ratio of cured resins measured by weight of water absorbed at the percentage of the weight of cured resins.

^b Pencil hardness.

^c T_g , glass-transition temperature of cured resins.

^d $T\%$, entire light transmittance of cured resins.

^e US, the onset wavelength of total absorption.

^f YI, yellowness index of the cured resins.

RESULTS AND DISCUSSION

Cured BEPTES/ESDGEBA resins

The curing monomers used in this work are listed in Table I. It can be seen that the episulfide monomer of BEPTES is a long-chain aliphatic compound, and the ESDGEBA is a aromatic group-containing compound. Thus the copolymerization of BEPTES with ESDGEBA can improve the heat resistance and mechanical properties of the optical resins.

The properties of the cured BEPTES/ESDGEBA resins are summarized in Table II. The cured BEPTES/ESDGEBA resins have a higher refractive index, and the Abbe's number is still higher. This indicates that the BEPTES/ESDGEBA cured resins exhibit well-balanced optical properties. The refractive index of the BEPTES homopolymer resin reached about 1.70 because of its higher sulfur content (53.7%). The refractive index (n_d) and Abbe's number (ν_d) increased linearly with the increase of the content of BEPTES

monomer (Fig. 1); thus the BEPTES monomer is a good copolymerization monomer for the enhancement of n_d and ν_d at the same time. The ESDGEBA homopolymerization resin is not obtained because of its higher melting point (89–90°C). The refractive index and Abbe's number of the ESDGEBA homopolymerization resin were obtained as 1.625 and 33.45, respectively, by linear regression analysis for the extrapolation to 0 wt % BEPTES.

The relationship between the density of the cured BEPTES/ESDGEBA resins and the weight content of BEPTES monomer was examined. The density of the cured resins increased with the content of BEPTES from 1.241 to 1.354 g/cm³ (Table II). This was brought about by the increase of content of sulfur elements, which have a higher specific gravity. The water-absorption ratio (Rwa) increased with the increase of the BEPTES content in resins, but it is still relatively small. The glass-transition temperature (T_g) of the BEPTES homopolymer resin is relatively lower, 65°C, compared with that of the copolymerization resins for the low BEPTES content. T_g of the cured resin with 10 wt % of BEPTES reached 150°C. In addition, the surface hardness of the resins also exhibits the same trend similar to that of T_g (Table II). Thus the ESDGEBA monomer can improve the thermal properties and mechanical properties of the copolymerization resins, which is in accordance with our initial design intention.

The transmittances of the cured resins are about 80%, The highest reached to 86% for the cured resins with 75 wt % of BEPTES. The onset total-absorption wavelengths of these resins are higher than that of PMMA (290 nm) and PS (310 nm), and they shift toward the longer wavelength when the content of ESDGEBA increased. This is closely related to the structure of the cured resins.²⁸

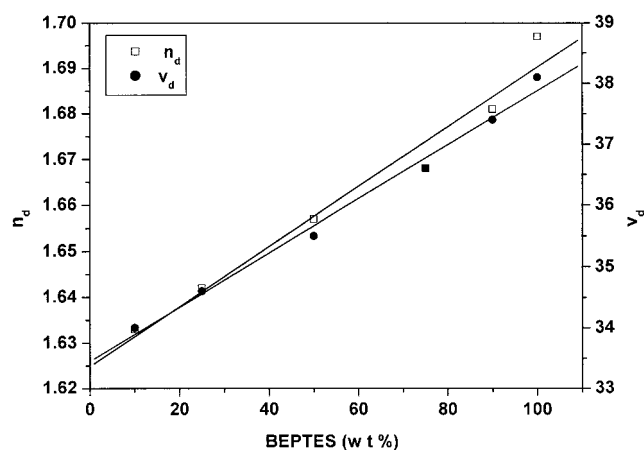


Figure 1 Variation of refractive index and Abbe's number of BEPTES/ESDGEBA resins with the content of BEPTES.

TABLE III
Properties of Cured BEPTES/TDI Resins

BEPTES/TDI (molar ratio)	n_d^{20}	ν_d	ρ (g/cm ³)	Rwa^a (wt %)	Hard ^b	T_g^c (°C)	$T\%^d$	US ^e (nm)	YI ^f
0.29	1.6520	28.7	1.2864	0.8799	4H	137	87	434	5.5
0.47	1.6543	29.4	1.2998	0.7044	4H	141	84	448	5.7
0.58	1.6569	30.2	1.3089	0.5501	4H	144	81	455	7.5
0.88	1.6621	32.0	1.3175	0.3167	4H	174	85	400	4.8
1.05	1.6649	33.3	1.3226	0.1343	5H	154	84	375	4.5
1.17	1.6694	34.6	1.3365	0.1208	5H	153	80	413	3.9

^a Rwa , water absorption ratio of cured resins measured by weight of water absorbed at the percentage of the weight of cured resins.

^b Pencil hardness.

^c T_g , glass-transition temperature of cured resins.

^d $T\%$, entire light transmittance of cured resins.

^e US, the onset wavelength of total absorption.

^f YI, yellowness index of the cured resins.

Cured BEPTES/TDI resins

Similar to epoxy resin, episulfide compound can also react with diisocyanate to form thermosetting resin. However, in the experimental studies, it was found that the aromatic diisocyanate (TDI) can easily react with BEPTES, whereas the aliphatic diisocyanate such as isophorone diisocyanate (IPDI) cannot, which may be the result of the isocyanate groups of the TDI molecule having a higher activity because of the conjugative effect of the benzene ring. In addition, as the molar ratio of BEPTES to TDI in the composition of copolymerization resins exceeds 1.17 or is less than 0.29, the cured resins with good properties cannot be obtained. Thus only the cured resins with the molar ratio of BEPTES to TDI ranging from 0.29 to 1.17 were prepared and their properties are listed in Table III.

These series of cured resins also have a high refractive index, although they are lower than that of the BEPTES/ESDGEBA system. Because the benzene rings of TDI exhibit larger dispersion, the cured resins

have low Abbe's numbers. Figure 2 shows that both refractive index and Abbe's number of the cured resins increase linearly with the increase of the molar ratio of BEPTES to TDI, whereas the refractive index change is small compared with the above system. The effects of molar ratio change of BEPTES to TDI on the density (ρ) and water-absorption ratio (Rwa) of BEPTES/TDI cured resins are shown in Figure 3. It can be seen that the densities of this system also increase with the increase of BEPTES content, whereas the water-absorption ratio of the system decreases. It can thus be deduced that higher contents of TDI made the cured resins more hydrophilic because of the polar bond formed in curing resins. However, the structure of the resulting cured resins is relative to the ratio of BEPTES to TDI, the same as in the epoxy-isocyanate system.²⁹⁻³¹ During the reaction of episulfide with TDI the poly(isocyanurate) and thiazolidone structures may be formed, which possess a good heat re-

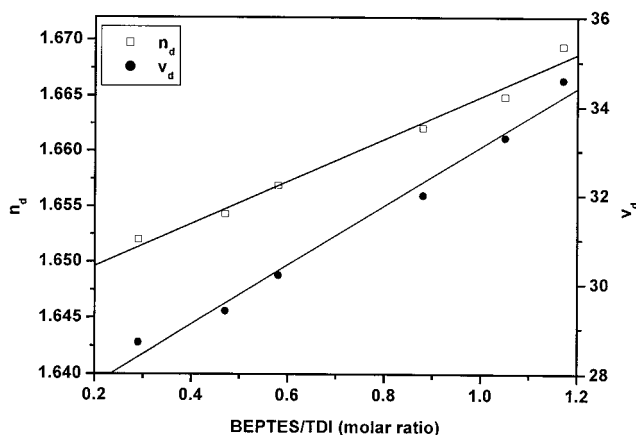


Figure 2 Variation of refractive index and Abbe's number of cured BEPTES/TDI resins with the increase of the molar ratio of BEPTES/TDI.

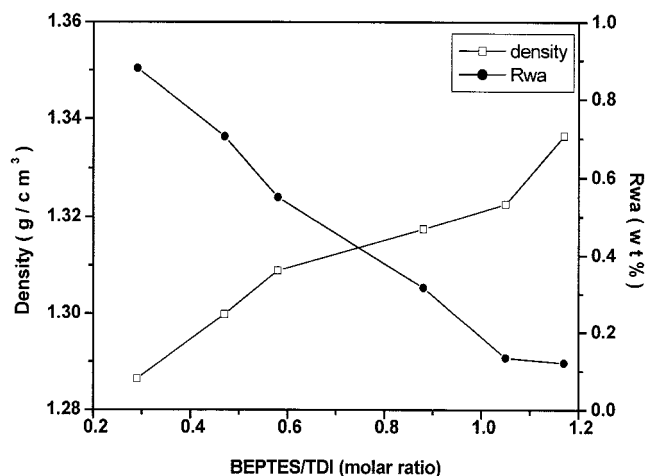


Figure 3 Effect of molar ratio change of BEPTES/TDI on the density (ρ) and water-absorption ratio (Rwa) of cured BEPTES/TDI resins.

sistance. As shown in Table III, the cured BEPTES/TDI resins have high glass-transition temperature ($T_g > 130^\circ\text{C}$) and surface hardness (4H–5H). When the molar ratio of BEPTES to TDI reached 0.88, the cured resin exhibits a T_g value of 174°C . It seems that the cured resins have higher crosslinking density when the molar ratio of BEPTES to TDI is closer to 0.9. A further study is needed to confirm the detailed structure of the cured resins with various molar ratios of BEPTES to TDI. The transmittance of this system is above 80%. The onset wavelengths of total absorption of the cured resins shift to longer wavelength compared with that of the BEPTES/ESDGEBA system. This phenomenon has also been observed in the polythiourethane system for TDI/B-thiol.²⁸ It probably related to the benzene ring of the TDI molecule. In addition, the formation of poly(isocyanurate) and thiazolidone structures and their molar ratio may cause the shift of onset wavelengths of total absorption of the cured resins, and this also requires further studies.

CONCLUSIONS

The episulfide-type resins of BEPTES/ESDGEBA and BEPTES/TDI with high refractive index were synthesized by ring-opening copolymerization of the corresponding copolymerization monomers under the catalysis of the tertiary amine. The BEPTES/ESDGEBA cured resins have a higher refractive index, in the range from 1.63 to 1.7, larger Abbe's numbers, and both of them are increased linearly with the content of BEPTES. The introduction of ESDGEBA into the copolymerization system can improve both surface hardness and the T_g of the cured resins. For the BEPTES/TDI system, the refractive indices and Abbe's numbers increase linearly with the increase of molar ratio of BEPTES to TDI. The system has higher surface hardness and T_g , particularly for the cured resins with the ratio of BEPTES to TDI closer to 0.9. In conclusion, these episulfide-type optical resins exhibit a higher refractive index, low dispersion, and well-balanced physical properties. It was considered to be another type of optical materials that will find wide practical applications, as successors to the polythiourethane resins.

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